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(54) Title: HAIR CARE COMPOSITIONS PROVIDING CONDITIONING AND ENHANCED SHINE		
(57) Abstract  Hair care compositions providing conditioning and enhanced shine to the hair comprising the combination of a <u>high refractive index nonvolatile polysiloxane fluid</u> , a <u>nonvolatile spreading agent</u> which is compatible with the polysiloxane fluid, and a <u>carrier</u> suitable for application to the hair. More specifically, provided is a hair care composition that comprises: (i) a mixture of (a) a nonvolatile polysiloxane fluid having a refractive index of at least about 1.46, such as a highly aryl-substituted polysiloxane fluid; and (b) a <u>nonvolatile spreading agent</u> for said silicone fluid intermixed with said polysiloxane fluid; and (ii) a <u>carrier</u> suitable for application to the hair.		

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## HAIR CARE COMPOSITIONS PROVIDING CONDITIONING AND ENHANCED SHINE

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### TECHNICAL FIELD

This invention relates to hair care compositions that provide conditioning and shine to the hair. More particularly, this invention relates to hair care compositions that provide conditioning and enhanced levels of shine to the hair.

### BACKGROUND OF THE INVENTION

The shampooing of hair conventionally is performed utilizing any of numerous detergent surfactant-containing compositions known in the art. Whereas it is well known how to formulate shampoos that can efficiently clean the hair, merely providing clean hair is not, in and of itself, satisfying to substantial segments of consumers who also want their hair to be manageable, and to also feel and look pleasing and healthy.

One common method of providing a more pleasing and manageable hair is through the use of hair conditioning agents, such as cationic, quaternary ammonium surfactants and polymers, silicone fluids, and hydrocarbon or other organic oils.

A common way to improve the appearance of hair is through the use of hair shine actives, such as shellac, dimethicone, oils and waxes, and quaternary ammonium surfactants. Some hair care ingredients, such as the oils and waxes, dimethicone, and cationic surfactants, provide conditioning as well as hair shine benefits. However, they can only be used at limited levels without causing adverse effects on hair appearance or feel. Too much oil, for example, can cause the hair to appear and feel greasy. High levels of dimethicone, cationic surfactants, and waxes can cause the hair to develop a dirty, coated feel and to become limp and without body, especially upon repeated usage. Shellac, on the other hand, causes the hair to feel stiff or tacky.

The purpose of hair shine actives is to increase the amount of light reflecting off the hair surface. The definition of hair shine is generally accepted to be the contrast between the specular and diffuse light reflected off the hair fibers. This contrast creates a perception of "sheen" or "highlights" strongly associated by the consumer with "healthy hair".

Whereas a wide variety of hair shine actives are known in the art, such as those discussed above, it remains highly desirable to provide hair care compositions that can provide enhanced levels of shine to the hair without incurring the cost, formulation difficulties, or hair aesthetic disadvantages that would be associated with merely increasing the level of hair shine active in prior-known compositions. It is an object of this invention to provide such hair care compositions.

It would further be desirable to provide hair care compositions that could provide enhanced shine, as described above, which could also provide conditioning the hair, especially improved combing and hair feel. It therefore is also an object of this invention to provide hair care compositions that can provide both conditioning and enhance shine to the hair.

These and other benefits as may be discussed or apparent to one of ordinary skill in the art can be provided according to the invention which is described below.

All percentages herein are by weight of the composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. Unless otherwise indicated, all percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products.

The invention hereof can comprise, consist of, or consist essentially of the essential elements described herein as well as any of the preferred or other optional ingredients described hererin.

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#### SUMMARY OF THE INVENTION

It has now been found that hair care compositions providing conditioning and enhanced shine to the hair are provided through the combination of a high refractive index nonvolatile polysiloxane fluid, a nonvolatile spreading agent which is compatible with the polysiloxane fluid, and a carrier suitable for application to the hair. It is essential that the compositions contain the spreading agent because even though the polysiloxane fluids hereof have high refractive index, they do not provide the high levels of shine obtainable with the present invention without the presence of the spreading agent.

More specifically, the present invention provides a hair care composition that comprises:

(a) a nonvolatile polysiloxane fluid having a refractive index of at least about 1.46;

5 (b) a nonvolatile spreading agent for said silicone fluid intermixed with said polysiloxane fluid; and

(c) a carrier suitable for application to the hair;

wherein said composition contains a sufficient amount of said spreading agent to reduce the Surface Tension of the polysiloxane fluid. Preferably, the Surface  
10 Tension is reduced by at least about 5%, more preferably by at least about 10%, and the total of the mixture of said polysiloxane fluid and said spreading agent is at least about 0.1%, by weight, of the composition. Alternately, the present invention can be described in terms of containing a sufficient amount of said spreading agent to increase the Glossmeter Specular Reflectance for said mixture.  
15 relative to said polysiloxane fluid, by at least about  $\Delta 1.0\%$ .

In preferred embodiments, the polysiloxane fluid is a highly arylated silicone, especially a highly phenylated silicone such as pentaphenyl trimethyl trisiloxane or diphenyl methylphenyl siloxane copolymer, or diphenyl dimethyl siloxane copolymer.

20 Suitable spreading agents include, but are not necessarily limited to, silicone resins (especially MQ silicone resins), surfactants such as polyether siloxane copolymers and non-silicone-containing organic surfactants.

The present invention also relates to a method for providing conditioning and enhanced shine by applying the compositions hereof to the hair.

25 The compositions and methods of the present invention are advantageous for utilization in connection with a wide variety of hair care products including leave-on compositions, such as hair lotions, tonics, gels, mousses, sprays, etc., and rinse-off compositions, such as shampoos and hair rinses.

30 The present invention including various optional and preferred embodiments thereof, is described in more detail below.

### DETAILED DESCRIPTION OF THE INVENTION

The essential components and aspects of the invention, as well as various optional and preferred ingredients and embodiments of the invention, are  
35 described below.

#### High Refractive Index Nonvolatile Polysiloxane Fluid

The compositions of the present invention contain as an essential ingredient a nonvolatile polysiloxane fluid ("silicone fluid") having a refractive

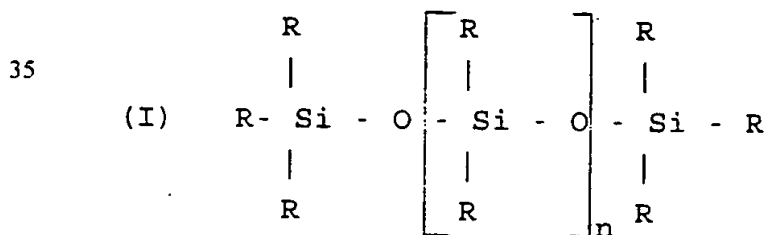
index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, most preferably at least about 1.55. Although not intended to necessarily limit the invention, the refractive index of the polysiloxane fluid will generally be less than about 1.70, typically less than about 1.60. Polysiloxane "fluid" includes fluids as well as gums.

As is well known in the art, refractive index refers to the change in direction (i.e. apparent bending) of a light ray passing from one medium to another. Refractive index shall herein refer to the light ray passing from air to the polysiloxane fluid or polysiloxane fluid/spreading agent mixture. Refractive index of the silicone fluid can be determined using standard equipment commonly available and known in the art, such as an Abbe refractometer. Techniques for measuring refractive index are described in the Handbook of Chemical Microscopy, Volume I - Chemical Methods and Inorganic Qualitative Analysis, Chemot and Mason, ed., John Wiley & Sons, Inc., New York, 1958, pp 311-334.

The term "nonvolatile" as used herein means the material referred to exhibits very low or no significant vapor pressure at ambient conditions, as well-known and understood in the art. Nonvolatile materials will generally exhibit no more than 0.2mm Hg at 25°C and one atmosphere. Nonvolatile materials will also generally have a boiling point at one atmosphere of at least 275°C, preferably at least 300°C.

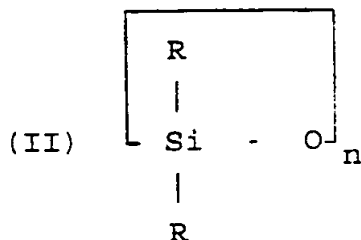
The polysiloxane fluid for use herein will generally have viscosity of at least about 10 centistokes at 25°C, preferably from about 20 to about 2,000,000 centistokes more preferably from about 30 to about 500,000 centistokes. Other viscosity nonvolatile silicone fluids can also be used in the present invention as long as the other requirements described herein are met. In general, if conditioning as well as hair shine is desired from the silicone fluid, higher viscosity materials such as those above about 50,000, preferably above about 100,000, are preferably used. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970.

The polysiloxane fluid suitable for purposes hereof includes those represented by general Formula (I):



wherein each R independently is substituted or unsubstituted aliphatic (e.g. alkyl or alkenyl), aryl, aryloxy, alkaryl, alkoxy, alkamino (e.g. alkyl or alkenyl amino groups), hydroxy, or hydrogen, or combinations thereof; and n is an integer of at least about 1, typically from about 1 to about 1,000. The R substituents can also include combinations of ether groups, hydroxy groups, and amine groups, as well as other functional groups, such as halogens and halogen-substituted functionalities, e.g. halogen-substituted aliphatic and aryl groups.

The polysiloxane fluid can be cyclic or linear. Linear polysiloxanes are exemplified above by Formula I. Branched chain can also be used. Cyclic polysiloxanes include those represented by Formula (II):



wherein R is as defined above,  $n$  is from about 3 to about 7, preferably from three to five.

The substituents on the siloxane chain (R) may have any structure as long as the resulting polysiloxanes remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, are capable of being deposited on the hair, and the resulting polysiloxane fluid has a refractive index as set forth above.

Preferred alkyl and alkenyl substitutes are  $C_1$ - $C_5$  alkyls and alkenyls, more preferably from  $C_1$ - $C_4$ , most preferably from  $C_1$ - $C_2$ . The aliphatic portions of other alkyl-, alkenyl-, or alkynyl- containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains and preferably have from one to five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to three carbon atoms, most preferably from one to two carbon atoms. As discussed above, the R substituents hereof can also, contain amine functionalities, e.g., alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di-, and tri- alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide), halogenated aliphatic or aryl groups, and hydroxy (e.g. hydroxy

substituted aliphatic groups). Suitable halogenated R groups could include, for example, tri-halogenated (preferably fluoro) alkyl groups such as  $-R^1-C(F)_3$ , wherein  $R^1$  is  $C_1-C_3$  alkyl. Examples of such polysiloxanes include polymethyl-3,3,3 trifluoropropylsiloxane.

5           The high refractive index polysiloxane fluids hereof contain a sufficient amount of aryl-containing R substituents to increase the refractive index to the desired level, which is described above.

          Aryl-containing substituents contain alicyclic and heterocyclic five and six membered aryl rings, and substituents containing fused five or six  
10   membered rings. The aryl rings themselves can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents, ketones, halogens (e.g., Cl and Br), amines, etc. Exemplary aryl-containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with  $C_1-C_5$  alkyl or  
15   alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl  $C_2-C_4$  alkynes). Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, naphthalene, coumarin, and purine.

20           In general, the polysiloxane fluids hereof will have a degree of aryl-containing substituents of at least about 15%, preferably at least about 20%, more preferably at least about 25%, even more preferably at least about 35%, most preferably at least about 50%. Typically, although it is not intended to necessarily limit the invention, the degree of aryl substitution will be less than  
25   about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

          The polysiloxane fluids hereof are also characterized by relatively high surface tensions as a result of their aryl substitution. In general, the polysiloxane fluids hereof will have a Surface Tension of at least about 24  
30   dynes/cm<sup>2</sup>, typically at least about 27 dynes/cm<sup>2</sup>. Surface Tension, for purposes hereof, is measured by a de Nouy ring tensiometer according to Dow Corning Corporate Test Method CTM 0461, November 23, 1971. Changes in Surface Tension can be measured according to the above test method or according to ASTM Method D 1331.

35           The preferred polysiloxane fluids hereof will have a combination of phenyl or phenyl derivative substituents (preferably phenyl), with alkyl substituents, preferably  $C_1-C_4$  alkyl (most preferably methyl) hydroxy, alkylamino



(especially  $-R^1NHR^2NH_2$  where each  $R^1$  and  $R^2$  independently is a  $C_1-C_3$  alkyl, alkenyl, and/or alkoxy.

High refractive index polysiloxane are available commercially from Dow Corning Corporation (Midland, Michigan, U.S.A.) Huls America (Piscataway, New Jersey, U.S.A.), General Electric Silicones (Waterford, New York, U.S.A.).

#### Spreading Agent

The compositions of the present invention will also comprise a nonvolatile spreading agent for the polysiloxane fluid. The spreading agent hereof must be compatible with the polysiloxane fluid.

The term "nonvolatile" is as defined previously herein. By "compatible" what is meant is that the spreading agent is soluble in, dispersible in, or miscible with the polysiloxane fluid, such that these two components can remain intermixed in the same phase of the composition. In other words, the spreading agent and the polysiloxane fluid are intermixed in the composition to form a mixture wherein the spreading agent reduces the Surface Tension of the polysiloxane fluid. Surface Tension reductions can be determined according to the procedure described previously herein. The spreading agent and polysiloxane fluid phase hereof can be a continuous or discontinuous phase in the present compositions.

In one aspect of the invention, the compositions hereof can be defined as containing contain a sufficient amount of the spreading agent to reduce the Surface Tension of the polysiloxane fluid by at least about 5%, preferably at least about 10%, more preferably at least about 15%, even more preferably at least about 20%, most preferably at least about 25%. Reductions in Surface Tension of the polysiloxane fluid/spreading agent mixture can provide improved shine enhancement of the hair. Although it is not intended to necessarily limit the maximum degree of Surface Tension reduction to any particular amount, in the preferred compositions hereof Surface Tension will generally be reduced by from about 20% to about 35%, more generally from about 25% to about 30%.

In general, the spreading agent should reduce the Surface Tension by at least about 2 dynes/cm<sup>2</sup>, preferably at least about 3 dynes/cm<sup>2</sup>, even more preferably at least about 4 dynes/cm<sup>2</sup>, most preferably at least about 5 dynes/cm<sup>2</sup>.

The Surface Tension of the mixture of the polysiloxane fluid and the spreading agent, at the proportions present in the final product, is preferably 30 dynes/cm<sup>2</sup> or less, more preferably about 28 dynes/cm<sup>2</sup> or less most preferably about 25 dynes/cm<sup>2</sup> or less. Typically the Surface Tension will be in the range of

from about 15 to about 30, more typically from about 18 to about 28, and most generally from about 20 to about 25 dynes/cm<sup>2</sup>.

Gloss is a physical attribute that contributes to the shine or lustrous appearance of an object. Gloss can be measured in terms of specular reflectance. Specular reflectance refers to the fraction, or percentage, of incident light reflected from a surface in the mirror direction (i.e. light reflected in the direction that is 180° from the light flowing from the light source toward the reflective surface) within a specified angular tolerance. Specular reflectance is a useful means for measuring shininess of hair. Further background in specular reflectance and its use in evaluating shininess of hair can be found in R. F. Stamm, M. L. Garcia, and J. J. Fuchs, "The Optical Properties of Human Hair-I. Fundamental Considerations and Goniophotometer Curves, and II. The Lustre of Human Hair Fibers," J. Soc. Cosmet. Chem. 28, 571-599 and 601-609 (September 1977) all incorporated herein by reference.

Specular reflectance measured from a coating of the compositions hereof on a collagen-coated black ceramic plate correlates with shininess on hair, and is less suspect to experimental variations due to inconsistency between hair samples and deposition the hair shine agent. Specular reflectance on such collagen-coated black ceramic plates as measured in the present invention is determined accordingly that the procedure below in the Experimental and is referred to herein as Glossmeter Specular Reflectance.

The present invention can alternately be described in terms of compositions containing a mixture of the spreading agent and the polysiloxane fluid wherein the composition contains a sufficient amount of the spreading agent to increase the Glossmeter Specular Reflectance for the mixture, relative to the polysiloxane fluid, by at least about "delta 1.0%" (hereinafter " $\Delta$  1.0%", wherein delta refers to a change in percentage specular reflectance based upon 100% of the original light intensity). Preferably, the increase in Glossmeter Specular Reflectance is at least about  $\Delta$ 2.0%, more preferably at least about  $\Delta$ 5.0%, even more preferably at least about  $\Delta$ 7.5%, most preferably at least about  $\Delta$ 10.0%.

Glossmeter Specular Reflectance is measured according to the procedure described below in the Experimental. In general, a 1.0% solution of the polysiloxane fluid in the same solvent, if any, used in the same phase as the polysiloxane fluid in the composition is used. If the polysiloxane fluid is not diluted with a separate solvent in the composition, cyclomethicone should be used to prepare the 1.0% solution. If the necessary cyclomethicone/ethanol solutions can be used to form the 1.0% of polysiloxane for purposes of the test. For the control, no spreading agent is incorporated. Otherwise, spreading agent is incorporated into the solution at the same weight ratio of polysiloxane fluid to spreading agent as present in the composition. The test solution is deposited on a collagen-coated, black ceramic tile and allowed to dry. Specular reflectance is measured with a glossmeter, a spectrophotometer suitable for measuring specular reflectance from flat surfaces. Suitable glossmeters are commercially available and known in the art, e.g. the "micro-gloss" glossmeter available from BYK-Gardner, Ind., Silver spring, MD, USA.

The weight ratio of the polysiloxane fluid to the spreading agent will, in general, be between about 1000:1 and about 1:10, preferably between about 100:1 and about 1:1, more preferably between about 50:1 and about 2:1, most preferably from about 25:1 to about 2:1. For hair rinse compositions it is particularly preferred for the ratio to be between about 10:1 and about 2:1. When fluorinated surfactants are used, particularly high polysiloxane: spreading agent ratios may be effective due to the efficiency of these surfactants. Thus, it is contemplated that ratios significantly above 1000:1 may be used.

Preferred spreading agents for use herein include silicone resins, and surfactants, which include both polyether siloxane copolymers and non-silicone-containing organic surfactants. Especially preferred spreading agents are the silicone resins.

Silicone Resin

Silicone resins are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional monomer units, or both, during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone resins will generally have at least about 1.1 oxygen atoms per silicon atom. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Typical silanes used in the manufacture of silicone resins are monomethyl-, dimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane. Preferred resins are the methyl substituted silicone resins, such as those offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in an unhardened form in a low viscosity volatile or, preferably, nonvolatile silicone fluid. The silicone resins for use herein will be present in the compositions hereof in non-hardened form rather than as a hardened resin, as will be readily apparent to those skilled in the art.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, and Chemistry and Technology of Silicones, Walter Noll, Academic Press, Inc. (Harcourt Bruce Javanovich, Publishers, New York), 1968, pp 282-287 and 409-426, both incorporated herein by reference.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit  $(\text{CH}_3)_3\text{SiO}_{1.5}$ , D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ , T denotes the trifunctional unit  $(\text{CH}_3)\text{Si}_{1.5}$ , and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical

alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins particularly those wherein the M:Q molar ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 500 to about 10,000, generally from about 1,000 to about 10,000.

Depending upon the particular choice of spreading agent (particularly the silicone resins) and polysiloxane fluid, it may be necessary or desirable to incorporate an additional solvent to ensure that the resin and polysiloxane fluid are compatible with one another. Thus, if the silicone resin isn't compatible with the polysiloxane fluid at the desired polysiloxane fluid : silicone resin weight ratio, it will be useful to incorporate into the polysiloxane/spreading agent phase a solvent to facilitate enhanced solubility or dispersibility of these components. If the solvent has a refractive index below about 1.46, or is otherwise below the refractive index of the polysiloxane fluid, it may be desirable to use a solvent which is volatile (materials that exhibit greater than 0.2mmHg at 25° C and one atmosphere, generally with a boiling point of less than 275° C), so that it does not remain on the hair and potentially impair the shine performance obtained according to the present invention. Suitable solvents include: cyclomethicone, other cyclic siloxanes such as those described herein as carrier fluids, linear polysiloxane polymers such as dimethicone, and other low viscosity analogues of the polysiloxane materials described in Formulas I and II, preferably having viscosity at 25° C of about 10 centistokes or less, such materials generally having lower (or zero) degree of aryl-containing substituents than the highly arylated, high refractive index polysiloxane of the present invention; volatile liquid hydrocarbons, such as straight or branched chain hydrocarbons having from about 4 to about 16 carbon atoms (e.g., hexane, isobutane, decane, dodecane, tetradecane, tridecane); lower alcohols (e.g. C<sub>2</sub>-C<sub>4</sub> alcohols such as ethanol and isopropanol); hydrocarbon esters, preferably with a total of about 10 carbon

atoms or less (e.g. ethyl acetate); halogenated hydrocarbons (e.g. freon); volatile ketones (e.g. acetone); and mixtures thereof. Especially preferred is cyclomethicone. The present invention does not, however, exclude the use of nonvolatile solvents for the resin/phenylated polysiloxane solvent.

When used, solvents as described above will be used typically at a weight ratio of (solvent) to (highly arylated nonvolatile polysiloxane plus spreading agent) of up to about 100:1, more typically up to about 50:1, for rinse-off hair care products, preferably from about 2:1 to about 10:1 for hair rinse products. For leave-on products, high levels of volatile solvents may be used as carrier ingredients, as described later.

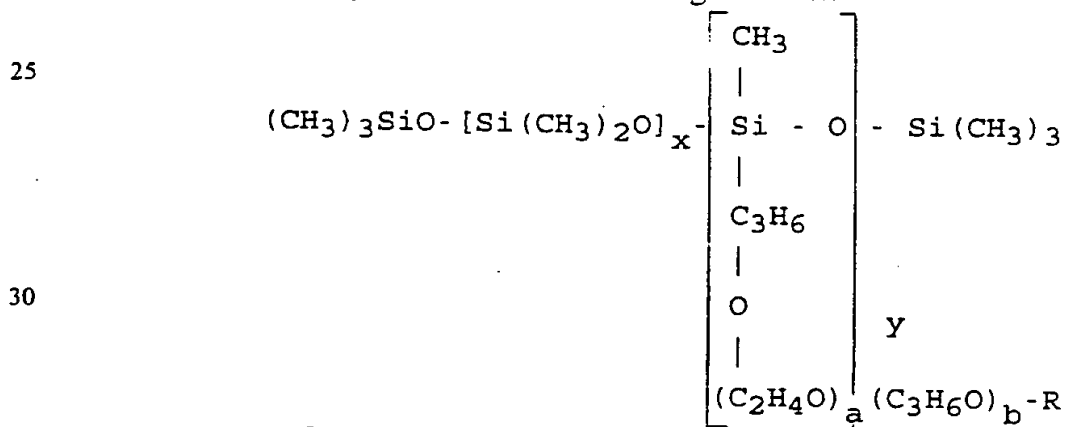
#### Surfactants

Surfactants that are compatible with the polysiloxane fluid hereof and which is suitable for application to the hair can also be used as a spreading agent. The surfactants can be anionic, cationic, nonionic, amphoteric, or a zwitterionic.

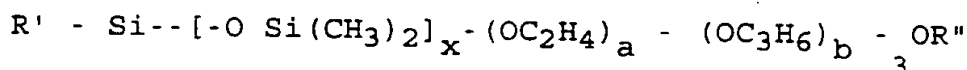
#### Polyether Siloxane Copolymer

Polyether siloxane copolymers, or silicone "copolyols" as they are sometimes referred to, are silicone-containing surfactants that can be utilized as spreading agents for the polysiloxane fluid. Silicone copolyols are surfactants characterized by a hydrophobic polysiloxane chain and a hydrophilic alkoxy portion.

Silicone copolyols which may be used include polyalkylene oxide modified polydimethylsiloxanes of the following formulae:



and



wherein R is hydrogen, an alkyl group having from 1 to about 12 carbon atoms, an alkoxy group having from 1 to about 6 carbon atoms or a hydroxyl group; R' and R'' are alkyl groups having from 1 to about 12 carbon atoms; x is an integer

of from 1 to 100, preferably from 20 to 30; y is an integer of 1 to 20, preferably from 2 to 10; and a and b are integers of from 0 to 50, preferably from 20 to 30.

Silicone copolyols among those useful herein are also disclosed in the following patent documents, all incorporated by reference herein: U.S. Patent 4,122,029, Geen, et al., issued October 24, 1978; U.S. Patent 4,265,878, Keil, issued May 5, 1981; and U.S. Patent 4,421,769, Dixon, et al., issued December 20, 1983. Such silicone copolyol materials are also disclosed, in hair compositions, in British Patent Application 2,066,659, Abe, published July 15, 1981 (incorporated by reference herein) and Canadian Patent 727,588, Kuehns, issued February 8, 1966 (incorporated by reference herein). Commercially available silicone copolyols which can be used herein, include Silwet Surface Active Copolymers (manufactured by the Union Carbide Corporation); and Dow Corning Silicone Surfactants (manufactured by the Dow Corning Corporation).

A variety of suitable non-silicone-containing organic surfactants that can be used are described below.

#### Anionic Surfactants

Anionic surfactants useful herein include alkyl and alkyl ether sulfates. These materials typically have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 10 to about 20 carbon atoms, x is 1 to 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine.

Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein  $\text{R}_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 12 to about 18, carbon atoms; and M is a cation. Important examples are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g.,  $\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ , oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $\text{C}_{12-18}$  n-paraffins.

Additional examples of anionic surfactants which come within the terms of the present invention are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived

from coconut oil. Other anionic surfactants of this variety are set forth in U.S. Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic surfactants include the class designated as succinamates. This class includes such surface active agents as disodium  
5 N-octadecylsulfosuccinamate; tetrasodium  
N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamate; diamyl ester of sodium  
sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl esters of  
sodium sulfosuccinic acid.

Other suitable anionic surfactants utilizable herein are olefin  
10 sulfonates having about 12 to about 24 carbon atoms. The term "olefin  
sulfonates" is used herein to mean compounds which can be produced by the  
sulfonation of a-olefins by means of uncomplexed sulfur trioxide, followed by  
neutralization of the acid reaction mixture in conditions such that any sultones  
which have been formed in the reaction are hydrolyzed to give the corresponding  
15 hydroxy-alkanesulfonates. The a-olefins from which the olefin sulfonates are  
derived are mono-olefins having about 12 to about 24 carbon atoms, preferably  
about 14 to about 16 carbon atoms. Another class of anionic organic surfactants  
are the b-alkyloxy alkane sulfonates.

#### Nonionic Surfactants

20 Nonionic surfactants can be broadly defined as compounds  
produced by the condensation of alkylene oxide groups (hydrophilic in nature)  
with a hydrophobic compound, which may be aliphatic or alkyl aromatic in  
nature. Examples of preferred classes of nonionic surfactants are:

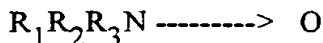
1. The polyethylene oxide condensates of alkyl phenols, e.g.,  
25 the condensation products of alkyl phenols having an alkyl group containing from  
about 6 to about 20 carbon atoms in either a straight chain or branched chain  
configuration, with ethylene oxide, the said ethylene oxide being present in  
amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of  
alkyl phenol.

30 2. Those derived from the condensation of ethylene oxide with  
the product resulting from the reaction of propylene oxide and ethylene diamine  
products.

3. The condensation product of aliphatic alcohols having from  
about 8 to about 18 carbon atoms, in either straight chain or branched chain  
35 configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide  
condensate having from about 10 to about 30 moles of ethylene oxide per mole of  
coconut alcohol, the coconut alcohol fraction having from about 10 to about 14  
carbon atoms.



4. Long chain tertiary amine oxides such as those corresponding to the following general formula:



wherein  $R_1$  contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R_2$  and  $R_3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals (the arrow in the formula represents a semipolar bond).

5. Long chain tertiary phosphine oxides corresponding to the following general formula:



wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and  $R'$  and  $R''$  are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. The arrow in the formula represents a semipolar bond.

6. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety.

7. Polysorbates, e.g., sucrose esters of fatty acids. Such materials are described in U.S. Patent 3,480,616, e.g., sucrose cocoate (a mixture of sucrose esters of a coconut acid, consisting primarily of monoesters, and sold under the tradenames GRILLOTEN LSE 87K from RITA, and CRODESTA SL-40 from Croda).

8. Alkyl polysaccharide nonionic surfactants are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group. The polysaccharide can contain from about 1.0 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of

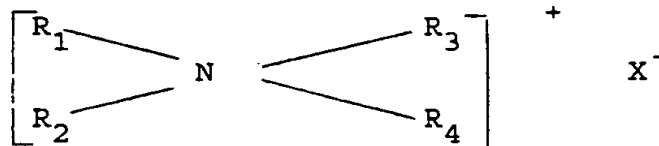
the additional saccharide units and the 2-, 3-, 4-, and/or 6-positions on the preceding saccharide units. Optionally there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The alkyl group preferably contains up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkylene moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-  
sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses.

9. Polyethylene glycol (PEG) glyceryl fatty esters, as depicted by the formula  $RC(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_nOH$  wherein  $n$  is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and  $RC(O)-$  is an ester wherein  $R$  comprises an aliphatic radical having from about 7 to 19 carbon atoms, preferably from about 9 to 17 carbon atoms, more preferably from about 11 to 17 carbon atoms, most preferably from about 11 to 14 carbon atoms. The combinations of  $n$  from about 20 to about 100, with  $C_{12}-C_{18}$ , preferably  $C_{12}-C_{15}$  fatty esters, for minimized adverse effect on foaming, is preferred.

#### Cationic Surfactants

Cationic surfactants useful in compositions of the present invention, particularly the conditioner compositions, contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein  $R_1-R_4$  are independently an aliphatic group of from about 1 to about 22 carbon atoms, or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having from about 12 to about 22 carbon atoms; and  $X$  is

an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, eg., those of about 12 carbons, or higher, can be saturated or

5

unsaturated.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or unsubstituted. Such amines, useful herein, include stearamido propyl dimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine. Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include

10

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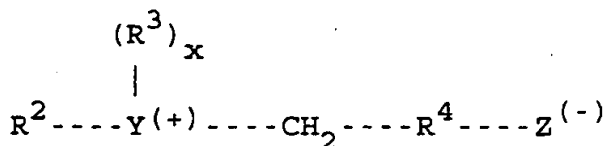
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#### Zwitterionic and Amphoteric Surfactants

Zwitterionic surfactants, useful in shampoos as well as conditioners, are exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:

25

30



35

wherein  $R^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $R^3$  is an alkyl or monohydroxyalkyl group containing about 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom;  $R^4$  is an alkylene or hydroxyalkylene of from about 1 to about 4 carbon atoms and Z is a radical selected from the

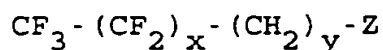
group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Other zwitterionics such as betaines are also useful in the present invention. Examples of betaines useful herein include the high alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, and lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine. The sulfobetaines may be represented by coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine and the like; amidobetaines and amidosulfobetaines, wherein the  $RCONH(CH_2)_3$  radical is attached to the nitrogen atom of the betaine are also useful in this invention.

Examples of amphoteric surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378, both of which patents are incorporated herein by reference.

Other surfactants that can be used include fluorosurfactants, or other halogenated surfactants, which can be anionic, nonionic, cationic, amphoteric, or zwitterionic.

Fluorosurfactants include perfluorinated compounds such as those represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to 17, particularly from 7 to 11, and y is an integer from 0 to 4, and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings

encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, each being incorporated herein by reference.

Fluorosurfactants, when used, will typically be used at lower levels than most other spreading agents. They will be used generally at weight ratios of polysiloxane fluid to spreading agent of from about 10,000:1 to about 1:1, preferably about 1,000:1 to about 10:1.

In general, the compositions hereof will contain from about 0.01% to 100% by weight of the spreading agent in admixture with the polysiloxane fluid, more generally from about 0.05% to about 50%, preferably from about 0.1% to about 15%, more preferably from about 0.2% to about 5%. any amount can be used as long as the compositions is effective for enhancing hair shine.

#### Carrier

The compositions of the present invention will comprise a carrier for the polysiloxane fluid and spreading agent suitable for application to the hair. The carrier is present at from 0% to about 99.99%, more generally from about 50% to about 99.95%, preferably from about 85% to about 99.9%, most preferably from about 95% to about 99.8%, of the composition. As used herein, the phrase "suitable for application to hair" means that the carrier does not damage or negatively affect the aesthetics of hair or cause irritation to skin. Choice of appropriate carrier will also depend on the particular polysiloxane fluid to be used, and whether the product formulated is meant to be left on the surface to which it is applied (e.g., hair spray, mousse, tonic) or rinsed off (e.g., shampoo, conditioner) after use.

The carriers used herein include solvents, as well as other carrier or vehicle components conventionally used in hair care compositions.

Suitable carrier fluids for use in the present invention include, but are not limited to, water, lower alcohols (e.g. C<sub>1</sub>-C<sub>6</sub>) monohydric alcohols, such as ethanol and isopropanol, hydroalcoholic mixtures, hydrocarbons (such as isobutane, hexane, decene, acetone), halogenated hydrocarbons (such as Freon), linalool, hydrocarbon esters (such as ethyl acetate, dibutyl phthalate), volatile silicon derivatives, especially siloxanes (such as phenyl pentamethyl disiloxane, methoxypropyl heptamethyl cyclotetrasiloxane, chloropropyl pentamethyl disiloxane, hydroxypropyl pentamethyl disiloxane, octamethyl cyclotetrasiloxane.

decamethyl cyclopentasiloxane, cyclomethicone, and dimethicone (having for example, viscosity at 25°C of about 15 centipoise or less), and mixtures thereof. Preferred carrier fluids include water, ethanol, volatile silicone derivatives, and mixtures thereof. The fluids used in such mixtures may be miscible or immiscible with each other.

The carrier may also include gel vehicle materials. The gel vehicle comprises two essential components: a lipid vehicle material and a cationic surfactant vehicle material. Cationic surfactant materials are described in detail above. Gel vehicles are generally described in the following documents, all incorporated by reference herein: Barry, "The Self Bodying Action of the Mixed Emulsifier Sodium Dodecyl Sulfate/Cetyl Alcohol", 28 J. of Colloid and Interface Science 82-91 (1968); Barry, et al., "The Self-Bodying Action of Alkyltrimethylammonium Bromides/Cetostearyl Alcohol Mixed Emulsifiers; Influence of Quaternary Chain Length", 35 J. of Colloid and Interface Science 689-708 (1971); and Barry, et al., "Rheology of Systems Containing Cetomacrogol 1000 - Cetostearyl Alcohol, I. Self Bodying Action", 38 J. of Colloid and Interface Science 616-625 (1972). Gel vehicles are particularly useful for hair rinse compositions, as well as leave-on hair care compositions such as gel conditioners and shine enhancers.

The carrier may also incorporate one or more lipid vehicle materials which are essentially water-insoluble, and contain hydrophobic and hydrophilic moieties. Lipid vehicle materials include naturally or synthetically-derived acids, acid derivatives, alcohols, esters, ethers, ketones, and amides with carbon chains of from about 12 to about 22, preferably from about 16 to about 18, carbon atoms in length. Fatty alcohols and fatty esters are preferred; fatty alcohols are particularly preferred.

Lipid vehicle materials among those useful herein are disclosed in Bailey's Industrial Oil and Fat Products, (3rd edition, D. Swern, ed., 1979), incorporated by reference herein. Fatty alcohols included among those useful herein are disclosed in the following documents, all incorporated by reference herein: U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 4,165,369, Watanabe, et al., issued August 21, 1979; U.S. Patent 4,269,824, Villamarin, et al., issued May 26, 1981; British Specification 1,532,585, published November 15, 1978; and Fukushima, et al., "The Effect of Cetostearyl Alcohol in Cosmetic Emulsions", 98 Cosmetics & Toiletries 89-112 (1983). Fatty esters included among those useful herein are disclosed in U.S. Patent 3,341,465, Kaufman, et al., issued September 12, 1976 (incorporated by reference herein). If included in the compositions of the present invention, the lipid vehicle material is

preferably present at from about 0.1% to about 10.0% of the composition; the cationic surfactant vehicle material is preferable present at from about 0.05% to about 5.0% of the composition.

Preferred lipids are esters, such as cetyl palmitate and glycerylmonostearate. Cetyl alcohol and stearyl alcohol are preferred alcohols. A particularly preferred lipid vehicle material is comprised of a mixture of cetyl alcohol and stearyl alcohol containing from about 55% to about 65% (by weight of mixture) of cetyl alcohol.

Preferred carriers for use in the compositions of the present invention, especially for hair rinses, include combinations of hydrophobically-modified hydroxyethyl cellulose materials with thickeners (such as locust bean gum), particular surfactants, quaternary ammonium compounds (such as ditallowdimethyl ammonium chloride), and/or chelating agents (such as EDTA). These vehicles are described in detail in the following patents: U.S. Patent 5,106,609, issued April 21, 1992 to Bolich et al., U.S. Patent 5,100,658, issued March 31, 1992 to Bolich et al., U.S. Patent 5,104,646, issued April 14, 1992 to Bolich et al., and U.S. Patent 5,100,657, issued March 31, 1992 to Ansher-Jackson et al., each incorporated herein by reference.

Suspending agents may also be utilized as carrier components for suspending the polysiloxane fluid/spreading agent hair shine agent and/or other immisable or particulate ingredients (e.g. anti-static cationic surfactants which are insoluble in the composition, anti-dandruff actives (e.g. zinc pyridinethione), etc. A suspending agent can be particularly important in pourable liquid formulations, such as shampoos.

Exemplary suspending agents useful in the present compositions include any of several long chain acyl derivative materials or mixtures of such materials, such as long chain acyl derivatives, long chain amine oxides, and mixtures thereof, wherein such suspending agents are present in the composition in crystalline form. These suspending agents are described in U.S. Patent 4,741,855, Grote and Russell, issued May 3, 1988, incorporated herein by reference. Included are ethylene glycol esters of fatty acids having from about 16 to about 22 carbon atoms. Preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suspending agents found useful are alkanol amides of fatty acids, having from about 16 to about 22 carbon atoms, preferably about 16 to 18 carbon atoms. Preferred alkanol amides are stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain

fatty acids (e.g., stearyl stearate, cetyl palmitate, etc.); glyceryl esters (e.g., glyceryl distearate) and long chain esters of long chain alkanol amides (e.g., stearamide DEA distearate, stearamide MEA stearate).

Still other suitable suspending agents are alkyl (C<sub>16</sub>-C<sub>22</sub>) dimethyl  
5 amine oxides such as stearyl dimethyl amine oxide. If the compositions contain an amine oxide or a long chain acyl derivative as a surfactant the suspending function could also be provided by such surfactant and additional suspending agent may not be needed if the level of those materials are at least the minimum level given below.

10 Other long chain acyl derivatives that can be used include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na and K salts), particularly N,N-di(hydrogenated) C<sub>16</sub>, C<sub>18</sub> and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

15 The long chain acyl derivative materials, when utilized as the suspending agent, are typically present in pourable, liquid formulations at a level of from about 0.1% to about 5.0%, preferably from about 0.5% to about 3.0%. The suspending agent serves to assist in suspending the silicone material and may give pearlescence to the product. Mixtures of suspending agents are also suitable  
20 for use in the compositions of this invention.

Another type of suspending agent that can be used is xanthan gum. Compositions utilizing xanthan gum as a suspending agent for a silicone hair conditioning component are described in U.S. Patent 4,788,006, Bolich and Williams, issued November 29, 1988, incorporated herein by reference. Xanthan  
25 gum is biosynthetic gum material that is commercially available. It is a heteropolysaccharide with a molecular weight of greater than 1 million. It is believed to contain D-glucose, D-mannose and D-glucuronate in the molar ratio of 2.8:2.0:2.0. the polysaccharide is partially acetylated with 4.7% acetyl. This information and other is found in Whistler, Roy L. Editor Industrial Gums - Polysaccharides and Their Derivatives New York: Academic Press, 1973. Kelco,  
30 a Division of Merck & Co., Inc. offers xanthan gum as KeltrolR. The gum, when used as the silicone hair conditioning component suspending agent, will typically be present in pourable, liquid formulations at a level of from about 0.3% to about 3%, preferably from about 0.4% to about 1.2% in the compositions of the present  
35 invention.

Combinations of long chain acyl derivatives and xanthan gum are disclosed as a suspending agent for silicone hair conditioners in U.S. Patent 4,704,272, Oh et al., issued November 3, 1987, incorporated herein by reference.



and may also be used in the present compositions. Gel formulations have high levels of suspending agent relative to pourable, liquid formulations when used as the primary means of imparting the gel-like viscosity to the composition. In such compositions, the suspending agent will typically be present at levels of from about .1 to about 5%. Alternately, other materials can be used to impart a gel-like viscosity to the composition, such as gelling agents (e.g., hydroxyethyl cellulose), thickeners, viscosity modifiers, etc. Mixtures of these materials can also be used.

Hair care compositions for which the present invention can be useful for also include, for example, tonics, mousses, gels and hair sprays. Tonics, gels and non-aerosol hair sprays utilize a solvent such as water or alcohol while mousses and aerosol hair sprays additionally utilize a propellant such as trichlorofluoromethane, dichlorodifluoromethane, difluoroethane, dimethylether, propane, n-butane or isobutane. A tonic or hair spray product having a low viscosity may also utilize an emulsifying agent. Examples of suitable emulsifying agents include nonionic, cationic, anionic surfactants, or mixtures thereof. If such an emulsifying agent is used, it is preferably present at a level of from about 0.01% to about 7.5% of the composition. The level of propellant can be adjusted as desired but is generally from about 3% to about 30% of mousse compositions and from about 15% to about 50% of the aerosol hair spray compositions.

Suitable spray containers are well known in the art and include conventional, non-aerosol pump sprays i.e., "atomizers," aerosol containers or can having propellant, as described above, and also pump aerosol containers utilizing compressed air as the propellant. Pump aerosol containers are disclosed, for example, in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStegge, both incorporated by reference herein, and also in U.S. Serial No. 07/839,648, Gosselin, Lund, Sojka, and Lefebvre, filed February 21, 1992, "Consumer Product Package Incorporating A Spray Device Utilizing Large Diameter Bubbles. Pump aerosols hair sprays using compressed air are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON AIRSPRAY<sup>R</sup> hair sprays.

#### Optional Ingredients

The compositions of the present invention may be formulated in a wide variety of product types, including mousses, gels, lotions, tonics, sprays, shampoos and conditioners. The additional components, in addition to the carrier, required or desirable to formulate such products vary with product type and can be routinely chosen by one skilled in the hair care product art. For example, shampoos, will also contain cleansing surfactants, a wide variety of

which are well known. Exemplary surfactants that can be used as cleansing surfactants are described above. These include anionic, nonionic, amphoteric, and zwitterionic non-silicone-containing surfactants. Hair conditioners may contain, in addition to the high refractive index polysiloxane fluids, other hair conditioning agents such as lower refractive index silicone fluids, such as those described herein but with lower degrees of aryl-substitution, e.g., dimethicone, cationic surfactants and cationic polymers, organic oils and waxes such as hydrocarbon oils, and fatty acid esters, and alcohols.

A particular category of low refractive index (i.e. refractive index below 1.46, generally below about 1.44, preferably from about 1.38 to about 1.42) polysiloxane fluids that can be used are polysiloxane gums. "Polysiloxane gum" refers to silicone fluids having a viscosity at 25°C of 1,000,000 cp or higher. Preferably, the viscosity will be from 1,000,000 to about 100,000,000 cp at 25°C. Especially preferred is polydimethylsiloxane gum. Low refractive index polysiloxane conditioners are generally used at levels of from about 0.01% to about 10%, by weight, of the compositions, preferably from about 0.1% to about 5%, more preferably from about 0.5% to about 5%, most preferably from about 1% to about 4%.

In addition to providing hair conditioning benefits to compositions containing the high refractive index and spreading agent hereof, it has been found that the combination of low refractive index polysiloxane gum and high refractive index polysiloxane fluids hereof, even in the absence of spreading agent, can provide excellent hair conditioning with surprising improvements in shine. The low refractive index polysiloxane gum and high refractive index polysiloxane fluid are used at the previously disclosed levels. The weight ratio for the low refractive index gum to the high refractive index fluid in this aspect of the invention is from about 1:100 to about 100:1, preferably from about 1:10 to about 10:1, more preferably from about 1:5 to about 5:1.

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C<sub>1</sub>-C<sub>7</sub> alkyl groups, more preferably C<sub>1</sub>-C<sub>3</sub> alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol and ethylene glycol. Other cationic polymers include cationic-modified polysaccharides, such as cationic ammonium modified cellulose. Suitable cationic

surfactants are generally described above, especially preferred are di(C<sub>12</sub>-C<sub>18</sub>, especially C<sub>16</sub>-C<sub>18</sub>) alkyl and alkenyl, dimethyl ammonium salts (especially chloride salts).

5 Hair setting compositions, e.g. sprays, mousses, gels, and hair rinses, can contain film forming polymers, i.e. adhesive polymers, as are well known in the art.

Exemplary adhesive polymers include polyvinylpyrrolidone (PVP), particularly poly N-vinyl pyrrolidone, copolymers of PVP and methylmethacrylate, copolymers of PVP and vinyl acetate (VA), and polyvinyl alcohol (PVA).

10 Exemplary adhesive polymers also include copolymers of VA and crotonic acid, copolymers of methylvinylether and maleic hemiesters (e.g. maleic ethyl ester and maleic butyl ester), hydroxypropyl cellulose, hydroxypropyl guar gum, polystyrene sulfonate salts, polyacrylic polymers such as polymers and copolymers of acrylic acid and methacrylic acid, co- and ter- polymers of acrylic  
15 acid and/or methacrylic acid with acrylamide and/or vinyl pyrrolidone such as terpolymers of vinyl pyrrolidone/methyl methacrylate/methacrylic, terpolymers of vinyl pyrrolidone/ethylmethacrylate/methacrylic acid, terpolymers of t-butyl acrylamide/ethyl acrylate/acrylic acid, and terpolymers of VA/crotonic acid/vinyl neodecanoate.

20 Other examples of anionic hair hold polymers are crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate; and copolymers of methyl vinyl ether and maleic anhydride (e.g. molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated aliphatic alcohol containing from 1 to 4 carbon atoms such as ethanol or  
25 butanol; and acrylic copolymers and terpolymers containing acrylic acid or methacrylic acid as the anionic radical-containing moiety such as copolymers with, butyl acrylate, ethyl methacrylate, etc.

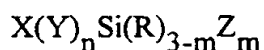
Polymeric hair hold polymers also include amphoteric polymers. One class of amphoteric polymers that can be used are acrylic resins with both  
30 cationic and carboxylic groups. Examples include terpolymers of octyl and acrylamide/acrylic acid/ butylaminoethyl methacrylate, copolymers of acrylic acid/betaine methacrylate, and copolymers of octylacrylamide/acrylates.

Also silicone grafted adhesive copolymers can be used, such as those described in which are polysiloxane-containing monomers with  
35 non-polysiloxane-containing monomers such that said adhesive agent has a weight average molecular weight of at least about 20,000, and comprises from about 1% to about 50%, by weight, of the polysiloxane-containing monomers.

The most preferred polymers comprise an organic backbone.

especially a carbon backbone such as a vinyl polymeric backbone, and also preferably, a polydimethylsiloxane macromer having a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000, is grafted to the backbone. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers. These include vinyl monomers, and other condensation monomers (eg., those that polymerize to form polyamides and polyesters) and ring-opening monomers (eg., ethyl oxazoline and caprolactone).

The preferred polymerizable polysiloxane-containing monomer (C monomer) can be exemplified by the general formula:



wherein X is a vinyl group copolymerizable with the A and B monomers; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C<sub>1</sub>-C<sub>4</sub>), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3.

Examples of useful polymers and how they are made are described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference.

Suitable polymers are also disclosed in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, and U.S. Serial No. 08/104,232, Bolich et al, filed August 10, 1993 all of which are incorporated by reference herein. Preferred of these polymers are copolymers comprising t-butyl acrylate and/or t-butyl methacrylate with vinyl monomers having polydimethylsiloxane macromers covalently attached thereto.

The compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art. e.g., pearlescent aids, such as ethylene glycol distearate; preservatives, such as benzyl

alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), cocomonoethanol amide, guar gum, methyl cellulose, starches and starch derivatives; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents, such as the thioglycolates; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin, disobutyl adipate, butyl stearate, and propylene glycol. Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0% of the composition.

The pH of the present compositions generally will be between about 3 and about 9, preferably between about 4 and about 8.

As with all compositions, the present invention should not contain components which unduly interfere with the performance of the compositions.

The hair care compositions of the present invention can be made using conventional formulation and mixing techniques. Exemplary methods of making various types of cosmetic compositions are also described more specifically in the Examples below.

#### Method of Use

The hair care compositions of the present invention are used in conventional ways to provide the conditioning and shine benefits of the present invention. Such method of use depends upon the type of composition employed but generally involves application of an effective amount of the product to the hair, which may then be rinsed from the hair or skin (as in the case of shampoos and some conditioning products) or allowed to remain on the hair (as in the case of spray, mousse, gel, lotion, and tonic products). By "effective amount" is meant an amount sufficient to provide a hair shine benefit. Preferably, hair rinse, mousse, and gel products are applied to wet or damp hair prior to drying of the hair. After such compositions are applied to the hair, the hair is dried and styled in the usual ways of the user. Hair sprays are typically applied to dry hair after it has already been dried and styled. Mousses, tonics and lotions are typically applied to hair in either dry or wet conditioning, depending upon the particular

intent of the formulation face, skin, or eye area in the conventional manners of usage for those types of products.

#### Experimental

The following procedure is used to determine Glossmeter Specular Reflectance.

5           A collagen solution is prepared by dissolving 10.0g of gelatin (175 bloom) in 83.0g DRO (double reverse osmosis) water at 155°C, with stirring. Next, 0.05g propylparaben is dissolved in the gelatin solution. Next, 4.5g 1M NaOH is added, followed by 3.0g of Ceraphyl GA-D (a mixture of 10-15% soy bean oil and 85-90% maleated soy bean oil available from VanDyk Inc.,  
10   Belleville, NJ, USA) to form a stable, white emulsion. Next, 1.2g of lactic acid is stirred into the emulsion, referred hereinafter as Solution A.

A 3.0%, by weight, formaldehyde in water solution, Solution B, is prepared and contained separately from Solution A.

Ceramic tiles, approximately 7.3cm x 7.3cm in size having a black  
15   glazed top and an average peak height ("roughness") of 5.0 - 7.0 microns (can be measured with a Rodenstock RM600-2D/3-D Measuring Station (Rodenstock Meterology, Munich, W. Germany)) are prepared and coated with the collagen on their top surfaces. Glossmeter Specular Reflectance of the collagen-coated tile should be from 8.0 - 12.0%.

20           Specular reflectance of the collagen-coated tile is measured utilizing a glossmeter, such as a BYK-Gardner "micro-gloss" glossmeter. Specular reflection measurements are made as described in ASTM Method D 523 at an angle of incidence of 60°. Specular reflectance as measured this way is referred to herein as "Glossmeter Specular Reflectance." The tiles can be  
25   prepared as follows. Syringe A is filled with 3.0cc of Solution A. Syringe B is filled with 0.2cc of Solution B. Syringe B contents are emptied onto the top surface of a tile. Syringe A contents are emptied onto the top of Solution B, on the top surface of the tile. The solutions are mixed for five seconds and spread uniformly on the top surface of the tile with a spatula. At 30 seconds after  
30   mixing, a 1.0 inch inside diameter metal ring is placed on the top surface of the tile. The collagen film is allowed to dry for eight hours. The metal ring is removed. The roughness of the collagen coated surface of the tile should be from 3.0 to 5.0 microns.

Polysiloxane and spreading agent mixtures are prepared, as  
35   described above, at a 1.00% concentration in a compatible diluent at a weight ratio of said polysiloxane fluid to said spreading agent corresponding to that found in the composition. A syringe is used to deposit 0.05cc of the mixture at the center of the area encompassed by the ring on the surface of the collagen-

coated tile. The mixture is allowed to dry. Glossmeter Specular Reflectance is measured.

### Examples

The following examples further illustrate preferred embodiments within the scope of the present invention. The examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

### PREMIX EXAMPLES 1-6

The following are a variety of exemplary polysiloxane fluid/spreading agent mixtures useful in the present invention. The mixtures can be used directly for treatment of the hair or, more preferably, can be used as components in a variety hair care compositions containing other cosmetically or pharmaceutically active ingredients, carrier ingredients, or other ingredients.

Component (Weight%)	Ex. 1	Ex. 2	Ex. 3
Pentaphenyl Trimethyl Trisiloxane (1)	57.00	0.00	50.00
Methylphenyl Diphenyl Siloxane Copolymer (2)	38.00	0.00	0.00
Diphenyl Dimethyl Siloxane Copolymer (3)	0.00	45.00	0.00
Dimethicone (4)	0.00	50.00	0.00
MQ Silicone Resin/Volatile Cyclomethicone (5)	5.00	5.00	0.00
Dimethicone Copolyol (6)	0.00	0.00	50.00
Fluorosurfactant (7)	0.00	1.00	0.00
Cyclomethicone (8)	0.00	0.00	0.00
Component (Weight%)	Ex. 4	Ex. 5	Ex. 6
Pentaphenyl Trimethyl Trisiloxane (1)	99.00	15.00	27.00
Methylphenyl Diphenyl Siloxane Copolymer (2)	0.00	0.00	12.00
Diphenyl Dimethyl Siloxane Copolymer (3)	0.00	0.00	0.00
Dimethicone (4)	0.00	0.00	0.00
MQ Silicone Resin/Volatile Cyclomethicone (5)	0.00	5.00	5.00
Dimethicone Copolyol (6)	0.00	0.00	0.00
Fluorosurfactant (7)	1.00	0.00	1.00
Cyclomethicone (8)	0.00	80.00	55.00

1. Dow Corning 705, Dow Corning
2. PS162, Huls
3. SF1265, General Electric

4. SE76, General Electric
5. SS4320, General Electric (50%/50% of polytrimethyl  
hydrosilylsilicate/decamethylcyclopentasiloxane)
6. Dow Corning 190, Dow Corning
7. FC-171 Fluorad, 3M
8. Dow Corning 344, Dow Corning

The premix is prepared by blending all the ingredients with agitation for about 1/2 hour at room temperature.

The following exemplary hair care compositions can be made utilizing any of the polysiloxane fluid/spreading agent premix Examples 1-6, above (hereafter referred to as "Silicone Premix Examples").

#### EXAMPLES I-III

The following are hair spray compositions representative of the present invention.

<u>Component</u>	<u>Example 3 (Weight %)</u>		
	<u>I</u>	<u>II</u>	<u>III</u>
Silicone Premix	4.5	4.5	4.5
Ethanol	79.0	79.0	86.4
Diisobutyl adipate	0.7	--	--
Potassium Hydroxide Solution (45% conc)	1.0	1.0	1.0
Perfume	0.2	0.2	0.2
Water	-----q.s. to 100%-----		

This product is prepared by dissolving the silicone premix to the ethanol and mixing for several hours until all of the premix is dissolved. Plasticizer is then added, if applicable. Potassium hydroxide is then added. Water or water/surfactant, as applicable, is added. Fragrance is added last. All ingredients are added under mixing conditions. The product can be packaged in conventional nonaerosol pump spray containers and compressed air pump spray aerosol containers.

#### EXAMPLE IV

The following is a hair grooming tonic composition representative of the present invention.

<u>Component</u>	<u>Weight %</u>
Silicone Premix	0.70
Perfume	0.10
Ethanol	q.s.



The composition is made by mixing the above components together in a conventional manner.

#### EXAMPLE V

The following is a shampoo composition representative of the

5 present invention.

<u>Component</u>	<u>Weight %</u>
Ammonium Lauryl Sulfate	4.00
Ammonium Laureth Sulfate	12.00
Ammonium Xylene Sulfonate	1.50
10 Ethylene Glycol Distearate	2.00
Cocomonoethanol Amide	2.00
Tricetyl Methyl Ammonium Chloride	0.50
Cetyl Alcohol	0.42
Stearyl Alcohol	0.18
15 Silicone Premix (see examples)	1.50
Preservative	0.03
Fragrance	1.20
Distilled Water	q.s.

Ammonium lauryl sulfate and citric acid are added to the  
 20 distilled water at about 15<sup>0</sup>C. The mixture is heated to from 70<sup>0</sup>C. to 80<sup>0</sup>C. The cocamide MEA and glycol distearate are added at this point. The ammonium laureth-3 sulfate, cetyl alcohol, stearyl alcohol and silicone premix are blended at from 70<sup>0</sup>C. to 90<sup>0</sup>C. This mixture is added to the batch following the glycol distearate. The preservative is then added. The batch is mixed for 5 minutes then  
 25 cooled to room temperature (15<sup>0</sup>C. to 25<sup>0</sup>C.). The fragrance is added. then the batch is milled under high shear for at least 5 minutes using conventional milling apparatus.

#### EXAMPLE VI

The following is a styling gel composition representative of the

30 present invention.

<u>Component</u>	<u>Weight %</u>
Silicone Premix	2.00
Carbopol 9401	0.75
Triethanolamine	1.00
35 Dye solution	0.05
Perfume	0.10
Laureth-23	0.10
DRO H <sub>2</sub> O	q.s.

- 1 cross-linked polyacrylic acid, commercially available from  
B. F. Goodrich

This batch is made by mixing the listed components together in  
a conventional manner.

5

### EXAMPLE VII

The following is a hair mousse composition representative of  
the present invention.

	<u>Component</u>	<u>Weight %</u>
	Silicone Premix	3.00
10	Ethanol	15.00
	Cocamine oxide	0.60
	Cocamide DEA	0.30
	Perfume	0.10
	Isobutane	7.00
15	DRO H <sub>2</sub> O	q.s.

- 1 dimethicone copolyol, commercially available from Dow Corning

The composition is made by blending all of the ingredients  
except isobutane at ambient temperature until well mixed. Aluminum aerosol  
cans are then filled with 95 parts of this batch, affixed with a valve which is  
20 crimped into position, and lastly pressure filled with 5 parts isobutane.

### Examples VIII-X

The following are conditioning rinse compositions  
representative of the present invention.

	<u>Component</u>	<u>Ex. VII</u>	<u>Ex. IX</u>	<u>Ex. X</u>
25	Hydroxethyl Cellulose	0.400	0.200	0.000
	Cetyl Hydroxyethylcellulose	0.000	0.400	0.500
	Croetin Q	1.000	1.000	1.000
	Stearylamidopropyl Dimethyl Amine	1.000	1.000	1.000
30	Ditallowdimethylammonium Chloride	0.750	0.750	0.750
	Glyceryl Monostearate	0.250	0.000	0.000
	Dipropylene Glycol Isoceteth-20 Acetate	0.000	0.250	0.250
	Cetyl Alcohol	0.900	1.700	1.700
	Stearyl Alcohol	0.600	0.000	0.000
35	Emulsifying Wax	0.500	0.000	0.000
	Octyl Methoxy Cinnamate	0.000	1.000	1.000
	Silicone Premix (see examples)	2.600	2.200	2.200
	Trimethyl silyl amodimethicone (1)	0.000	0.000	0.200

Fragrance	0.300	0.300	0.300
Citric Acid	0.220	0.220	0.220
Preservative	0.030	0.030	0.030
Distilled Water	q.s.	q.s.	q.s.

5

#### 1. Dow Corning Q2-8820, Dow Corning

Hydroxyethyl cellulose is added to the distilled water at a temperature of 15<sup>0</sup>C. to 40<sup>0</sup>C. This mixture is well dispersed, then heated to a temperature of from 60<sup>0</sup>C. to 90<sup>0</sup>C. Materials 2 through 10 are added to the batch while the temperature is maintained in this range. The mixture is stirred for approximately 10 minutes, then cooled to approximately 50<sup>0</sup>C. The remaining materials are added at this temperature. The mixture is milled under high shear for approximately 2 minutes using a conventional milling apparatus, then cooled to room temperature and collected. Alternatively the Silicone Premix components can be added at the same stage above, without premixing in advance.

15

#### EXAMPLE XI

An aerosol hair spray composition of the present invention is prepared as follows:

<u>Component</u>	<u>Weight %</u>
20 Silicone Premix	4.00
Water	10.60
Ethanol	63.50
KOH (45% solution)	0.90
Isobutane	15.00
25 Difluoroethane	6.00

All of the ingredients except for the propellants are mixed together at ambient temperature until the polymer is dissolved. The mixture is placed in an aerosol can which is then equipped with a conventional aerosol spray can valve which is vacuum crimped in place. The propellants are then filled through the valve and the can is equipped with a conventional aerosol spray can activator.

30

#### EXAMPLES XII-XV

Hair rinse compositions of the present invention are prepared as follows:

<u>Component (Wt.%)</u>	<u>Ex. XII</u>	<u>Ex. XIII</u>	<u>Ex. XIV</u>	<u>Ex. XV</u>
Oleyl Alcohol	1.0	1.0	1.0	0.2
Salcare <sup>R</sup> SC951	2.2	0.8	0.8	0.8
Trioctyldodecyl Citrate	1.0	-	-	-

35

		34			
	Polydimethylsiloxane <sup>2</sup>	3.5	4.2	4.2	4.2
	Silicone Resin <sup>3</sup>	0.2	0.2	0.2	0.2
	Pentaphenyl Trimethyl Trisiloxane <sup>4</sup>	0.4	0.4	0.4	0.4
	DL Panthenol	0.04	0.04	0.04	0.04
5	Panthenyl Ethyl Ether	0.3	0.3	0.3	0.3
	Fragrance	0.3	0.3	0.3	0.3
	Kathon™ CG <sup>5</sup>	0.03	0.03	0.03	0.03
	Hydroxypropyl Guar Gum	0.5	-	-	-
	Hydroxyethyl Cellulose	-	-	0.2	0.2
10	Cetyl Alcohol	-	1.2	1.8	1.8
	Stearyl Alcohol	-	0.8	1.2	1.2
	Ditallow Dimethyl Ammonium				
	Chloride	1.0	0.8	0.8	0.8
	Stearamidopropyl Dimethylamine	-	1.0	0.8	0.8
15	Glycerol Monostearate	-	0.2	0.8	0.8
	Citric Acid	-	0.2	0.2	0.2
	Water	q.s	q.s	q.s	q.s

- 1 Polyquaternium 37 (and) Mineral Oil (and) PPG-1 Trideceth 6, commercially available from Allied Colloids Ltd., (Norfolk, VA, USA).
- 20 2 An 85%/15% (wt. basis) mixture of D5 Cyclomethicone and dimethicone gum (weight average molecular weight of about 400,000 to about 600,000).
- 3 Polytrimethyl hydrosilylsilicate, added as a 50 wt.% solution in decamethylcyclopentasiloxane, General Electric Silicone Products, SS 4320.
- 4 Dow Corning 705, Dow Corning Corp. (Midland, MI, USA).
- 25 5 Methylchloroisothiazoline (and) methylisothiazoline, a preservative from Rohm & Haas Co., (Philadelphia, PA, USA).

For each of the examples, a silicone premix is prepared by mixing: the polydimethylsiloxane, MQ resin, and pentaphenyl trimethylsiloxane in a tank. For Example XII, the water is heated to about 80°C. The hydroxypropyl

30 guar gum and quaternary ammonium are sequentially added and mixed into the water. The batch is cooled to about 28°C. The following ingredients are then sequentially well mixed into the batch in the order given, with agitation between each addition: 1.0% (total wt. basis) Salcare™ SC95, trioctyldodecyl citrate, oleyl alcohol, panthenol, panthenyl ethyl ether, silicone premix, perfume, Kathon™ CG,

35 and the remainder of the Salcare™ SC95.

For Examples XIV and XV, the water is heated to about 25°C and the hydroxyethyl cellulose is added, with agitation. The water is heated to about 80°C and the following ingredients are sequentially added, with agitation

between each addition: quaternary ammonium salt, cetyl alcohol, stearyl alcohol, stearamidopropyl dimethylamine, and glyceryl monostearate. Cool the batch to about 49°C. Sequentially add the following ingredients with agitation between each addition: Silicone premix, citric acid, panthenol, panthenyl ethyl ether, perfume, Kathon™ CG, Salcare™ SC 95, and oleyl alcohol. Cool to 25°C.

For Example XIII, heat the water to about 80°C and mix into it the quaternary ammonium salt, with agitation. Next add the following ingredients sequentially with agitation between each addition: cetyl alcohol, stearyl alcohol, oleyl alcohol, stearamidopropyl dimethylamine, and glyceryl monostearate. Cool the batch to about 49°C. Next add the following ingredients with agitation between each addition: silicone premix, citric acid, panthenol, panthenyl ethyl ether, perfume, Kathon™ CG, and Salcare™ SC 95. Cool to 25°C.

## CLAIMS:

36

1. A hair care composition that provides enhanced shine to the hair, said composition characterized in that it comprises:

- (a) a nonvolatile polysiloxane fluid having a refractive index of at least 1.46;
- (b) a nonvolatile spreading agent for said polysiloxane fluid intermixed with said polysiloxane fluid; and
- (c) a carrier suitable for application to the hair;

wherein said composition contains a sufficient amount of said spreading agent to reduce the Surface Tension of the polysiloxane fluid by at least 5% and the total of said polysiloxane fluid and said spreading agent is at least 0.1%, by weight, of the composition.

2. A hair care composition as in Claim 1, wherein said mixture of polysiloxane fluid and spreading agent has a Surface Tension of  $30 \text{ dynes/cm}^2$  or less, preferably  $28 \text{ dynes/cm}^2$  or less, more preferably  $25 \text{ dynes/cm}^2$  or less, and said Surface Tension of the polysiloxane fluid is reduced by said spreading agent by at least 20%, preferably at least 25%.

3. A hair care composition that provides shine to the hair, said composition being characterized in that it comprises:

(i) a mixture comprising:

- (a) a nonvolatile polysiloxane fluid having a refractive index of at least 1.46;
- (b) a nonvolatile spreading agent for said silicone which is intermixed with said polysiloxane fluid, whereby said spreading agent reduces the surface tension of said polysiloxane fluid; and

(ii) a carrier suitable for application to the hair;

wherein said composition contains a sufficient amount of said spreading agent to increase Glossmeter-Specular Reflectance for said mixture, relative to said polysiloxane fluid, by at least  $\Delta 1.0\%$ .

4. A hair care composition as in Claim 3, wherein the glossmeter Specular Reflectance for said mixture is at least  $\Delta 2.0\%$  greater than the Glossmeter Specular Reflectance for said polysiloxane fluid, preferably, at least  $\Delta 5.0\%$ , more preferably at least  $\Delta 10.0\%$ .

5. A hair care composition that provides shine to the hair, said composition being characterized in that it comprises:

(i) a mixture comprising:

- (a) a nonvolatile polysiloxane fluid having a refractive index of at least 1.46;
- (b) a nonvolatile spreading agent selected from the group consisting of silicone resin surfactants, and mixtures thereof, wherein said spreading agent reduces the surface tension of said polysiloxane fluid;

(ii) a carrier suitable for application to the hair;

wherein said composition as a weight ratio of said polysiloxane fluid to said spreading agent of from 1000:1 to 1:10.

6. A hair care composition that provides shine to the hair, said composition being characterized in that it comprises:

(i) a mixture comprising:

(a) a nonvolatile polysiloxane fluid having a refractive index of at least 1.46;

(b) a nonvolatile spreading agent for said silicone which is intermixed with said polysiloxane fluid, whereby said spreading agent reduces the surface tension of said polysiloxane fluid; and

(c) a nonvolatile polysiloxane gum having a refractive index below 1.46, wherein the weight ratio of (a) to (c) is from 1:10 to 10:1;

(ii) a carrier suitable for application to the hair;

wherein said composition contains a sufficient amount of said spreading agent to increase Glossmeter Specular Reflectance for said mixture, relative to said polysiloxane fluid, by at least  $\Delta$  1.0%.

7. A hair care composition as in Claim 5 or 6, wherein said weight ratio of polysiloxane fluid to spreading agent is from 100:1 to 2:1, preferably from 50:1 to 2:1.

8. A hair care composition as in Claim 1, 2, 3, 4, 5, 6, or 7, wherein said nonvolatile polysiloxane fluid has a refractive index of at least 1.48, preferably at least 1.52, more preferably at least 1.55.

9. A hair care composition as in Claim 1, 2, 3, 4, 5, 6, 7, or 8, wherein said spreading agent is a silicone resin, preferably an MQ resin.

10. A hair care composition as in Claim 1, 2, 3, 4, 5, 6, 7, 8, or 9, wherein said nonvolatile polysiloxane fluid has a degree of aryl substitution of at least 20%, preferably at least 35%, more preferably at least 50%.

11. A hair care composition as in Claim 10, wherein said polysiloxane fluid has a degree of phenyl-containing substituents of at least 50%

12. A method for providing shine to the hair comprising applying the composition of Claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11, to the hair.

13. A method as in Claim 12, wherein said composition is rinsed from the hair after application to the hair.

14. A hair care composition that provides shine to the hair, said composition being characterized in that it comprises:

(i) a mixture comprising:

(a) a nonvolatile polysiloxane fluid having a refractive index of at least 1.46;

(b) a nonvolatile polysiloxane gum having a refractive index below 1.46, wherein the weight ratio of (a) to (b) is from 1:5 to 5:1.

(ii) a carrier suitable for application to the hair.



## INTERNATIONAL SEARCH REPORT

International Application No.

/US 93/09937

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 426 520 (L'OREAL) 8 May 1991 see the whole document ---	1,3,5,6, 12-14
P,Y	WO,A,93 19074 (PPG INDUSTRIES INC.) 30 September 1993 see page 2, line 26 - line 33; claims ---	1,3,5,6, 12-14
A	WO,A,92 10161 (THE PROCTER & GAMBLE COMPANY) 25 June 1992 see the whole document ---	1-14
A	EP,A,0 412 707 (THE PROCTER & GAMBLE COMPANY) 13 February 1991 see the whole document ---	1-14
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Int. Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP,A,0 400 976 (UNILEVER PLC) 5 December 1990 see the whole document ---	1-14
A	EP,A,0 240 350 (THE PROCTER & GAMBLE COMPANY) 7 October 1987 see the whole document ---	1-14
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